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TOWARDS UNSATURATED MACROCYCLIC STRUCTURES FROM POLYBUTADIENE WASTE STREAMS WITH RU METATHESIS CATALYSIS

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ABSTRACT

Large and unsaturated ring structures exhibit unique physical and chemical properties due to a dense conformation and the absence of chain ends. These structures could be implemented in applications like fragrances, high-performance lubricants, star shaped polymers and other specialty materials. Industrially produced unsaturated ring structures include cyclooctadiene (COD) and cyclododecatriene (CDT), small cycles of respectively 8 and 12 carbon atoms, synthesized by the cyclooligomerisation of 1,3-butadiene. Because of a lack of feasible synthesis methods, larger macrocycles are not produced. The cyclo-depolymerisation of polybutadiene by metathesis can provide a worthy route towards these larger macrocycles. Since polybutadiene is produced on a large scale, waste streams are readily available and cheap. Previous research performed by Thorn-Csanyi et al.[1],Chauvin et al.[2] and Suter et al.[3] with molybdenum and tungsten catalysts showed interesting results with respect to the thermodynamic equilibrium.

Here, we present an innovative process for the production of these larger macrocyclic structures with a ring size of C16-C44 carbon atoms. The obtained yield is greatly influenced by the type of the polybutadiene (molecular weight, abundance vinyl groups), reaction conditions (polymer concentration) and somewhat surprisingly the ligand environment of the Ru catalyst.

Study of the polybutadiene type highlighted the importance of a high-molecular weight polybutadiene lacking vinyl groups. By this, high yields (93 %) of ring structures were obtained. Equilibrium distributions are dominated by the all-trans CDT, which is economically a less relevant isomer. Although CDT is thermodynamically favored, it is a secondary reaction product from kinetically favored larger macrocycles, formed by tandem ring-opening ring-closing metathesis (RO-RCM). Further investigation of the reaction conditions on both equilibrium and kinetic product distributions clarified an optimal substrate concentration to maximize the kinetically formed macrocyles (C16-C44). Via a variation of the ligand environment of the Ru catalyst, the secondary formation of the thermodynamically stable CDT from the larger macrocycles could be efficiently suppressed (figure 1). Ru complexes lacking N-heterocyclic carbene ligands (e.g. Grubbs I, Umicore I) seemed to be the success factor. A pseudo-equilibrium with a yield of 86 % macrocycles (C16- C44) was finally achieved.

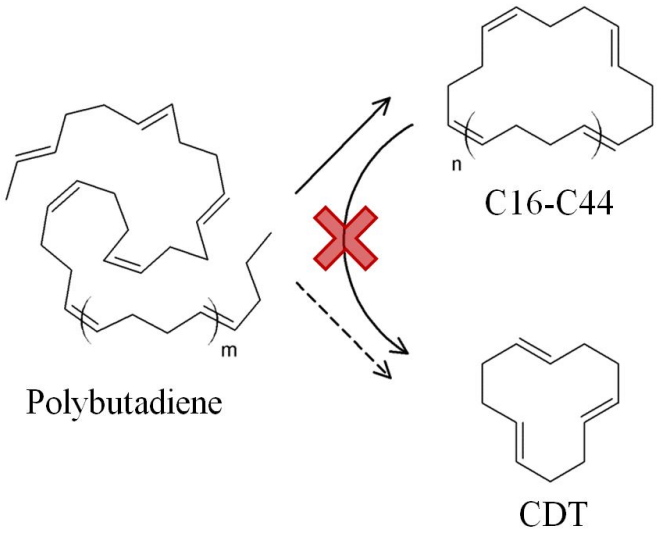

FIG1 LEGEND

Proposed reaction scheme for the formation of ring structures from polybutadiene.C16-C44 macrocycles are kinetic products and converted to mainly CDT via RO-RCM. The secondary reaction is suppressed (red cross) when using Ru catalysts lacking NHC-ligands.

FIG2 LEGEND

KEYWORDS

metathesis | ruthenium | macrocycles | polybutadiene | depolymerisation

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